Synthesis and Crystal Structure of a New Zinc(II) Coordination Polymer Assembled by 4-Nitrophthalic Acid and Bis(imidazol) Ligands

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ABSTRACT A new complex $[Zn(4\text{-nph})(bib)]_{2n}\cdot nH_2O$ (**1**) has been obtained by the reaction of metal (Zn(II)), 1,4-bis(imidazol-1-yl)-butane (bib) with 4-nitrophthalic acid (4-H_2nph). The crystal structure of **1** has been determined by single-crystal X-ray diffraction analysis. Compound **1** is of triclinic system, space group $P\bar{1}$ with a = 10.3251, b = 12.4503, c = 16.6497 Å, α = 88.487(3), β = 72.529(3), γ = 79.991(3)°, V = 2009.8(5) Å^3 and M_r = 945.47. Complex **1** shows a three-dimensional (3*D*) framework. Moreover, through intermolecular hydrogen bonds, compound **1** is assembled into a supramolecular structure. The thermal stability and luminescent properties of **1** are also investigated.

Keywords: Zn(II) coordination polymer; bis(imidazole) ligand; luminescent property; synthesis;

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1 INTRODUCTION

The current interest in coordination polymers (CPs) not only stems from their potential applications in gas storage[1], luminescence[2] and magnetism[3], but also from their intriguing variety of topologies and entanglement motifs[4]. The exploitation of various kinds of organic ligands is of vital importance to increase the structural diversity of coordination polymers, which meanwhile provides new insights into the relationships between the structure and the corresponding function. Among organic ligands, imidazole-containing ligands have been proven to be good candidates for the construction of new CPs due to their diverse coordination modes[5].

The carboxylate ligands have also received much attention in the designed synthesis of CPs due to their many coordination modes, such as monodentate, chelating and/or bridging, which allows a wide variety of structures[6]. In this paper, we use dicarboxylate and 1,4-bis(imidazol-1-yl)-butane ligand to construct a new Zn(II) coordination polymer, $[Zn(4\text{-nph})(bib)]_{2n} \cdot nH_2O$ (**1**). Complex **1** has a 3D framework and displays (4,4) topological net. Furthermore, the luminescent properties and TG of this complex were investigated in the solid state at room temperature.

2 EXPERIMENTAL

2. 1 Materials and instruments

All the chemicals were commercially purchased and used without further purification. Elemental analyses of C, H and N were performed on an Elementar Vario III Elemental Analyzer. IR spectrum was recorded in the range of 4000～400 cm^{-1} on a Nicolet 6700 spectrometer using a KBr pellet. Thermogravimetrical analyses (TGA) were performed on a Perkin-Elmer thermal analyzer under nitrogen at a heating rate of 10 ℃ min^{-1}. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ range of 5～50 °with a scan speed of 0.1 °S^{-1} on a Bruker D8 Advance instrument using a Cu$K\alpha$ radiation (λ = 0.154056 nm) at room temperature. The fluorescent studies were carried out on a computer-controlled JY Fluoro-Max-3 spectrometer at room temperature.

2. 2 Synthesis of $[Zn(4\text{-nph})(bib)]_{2n} \cdot nH_2O$

A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (0.2 mmol, 0.044 g), 4-H_2nph (0.04 g, 0.2 mmol) and bib (0.038 g, 0.2 mmol) was dissolved in 15 mL H_2O. The final mixture was placed in a Parr Teflon-lined stainless-steel vessel (25 mL) under autogenous pressure and heated at 130 ℃ for five days. The crystals of parallelogram were obtained. The yield of the reaction was ca. 28% based on Zn. Calcd. for $C_{36}H_{34}N_{10}O_{13}Zn_2$: C, 45.73; H, 3.62; N, 14.81%. Found: C, 45.21; H, 3.08; N, 14.32%. IR (KBr, cm^{-1}): 3462(w), 3139(w), 1630(s), 1521(m), 1342(m), 1099(w), 1060(w), 838(w), 722(w), 650(w).

2. 3 X-ray crystallographic study

A single crystal of the title compound with dimensions of 0.28mm × 0.10mm × 0.06mm was mounted on a Bruker Smart APEX II CCD diffractometer equipped with a graphite-monochromatic Mo$K\alpha$ (λ = 0.71073 Å) radiation using an ω scan mode at 293(2) K. In the range of $2.56<2\theta<52.16^o$, a total of 11046 reflections were collected and 7829 were independent with R_{int} = 0.0597, of which 3521 were observed with $I > 2\sigma(I)$. The

correction for *Lp* factors was applied. The structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares technique using the SHELXL-97 crystallographic software package[7]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The H atoms of coordinated water molecules were located from difference Fourier syntheses and the hydrogen atoms of organic ligands were generated geometrically. The final R = 0.0710 and wR = 0.1524 (w = $1/[\sigma^2(F_o^2) + (0.0840P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$). S = 0.962, $(\Delta\rho)_{max}$ = 0.712, $(\Delta\rho)_{min}$ = –0.590 e/Å^3 and $(\Delta/\sigma)_{max}$ = 0.000. The selected bond lengths and bond angles are listed in Table 1.

3 RESULTS AND DISCUSSION

3. 1 Crystal structure description of $[Zn(4\text{-nph})(bib)]_{2n} \cdot nH_2O$ (1)

Compound **1** crystallizes in triclinic crystal system with $P\bar{1}$ space group and features a three-dimensional (3*D*) network. The coordination environment of Zn(II) in **1** is shown in Fig. 1. There are two crystallographically unique Zn(II) centers, two 4-nph ligands, two bib ligands and one lattice water molecule in the asymmetric unit. Zn(1) and Zn(2) display the four-coordinated tetrahedral geometry with only different bond lengths and bond angles coordinated by two carboxylic oxygen atoms from two different 4-nph^{2-} ligands and two nitrogen atoms from two different bib ligands. The Zn–O bond distances fall in the 1.942(5)~1.981(5) Å range, and the Zn–N bond distances vary from 1.987(6) to 2.021(6) Å, which are all similar to those for other previously reported Zn(II) complexes[8].

The 4-nph and bib lignds exhibit a monodentate coordinate mode. Each 4-nph^{2-} ligand bridges the adjacent Zn(II) cations to yield binuclear subunits, which were linked by bib ligands to generate a *zigzag* double chain with the Zn(II) ··Zn(II) distances of 12.544 and 13.987 Å (Fig. 2). Then the 1*D* double chains are linked to form a 3*D* network by 4-nph^{2-} and bib ligands. From a topological viewpoint, the Zn(II) cations can be considered as (4,4) nodes (Fig. 3). Further, a 3*D* suparmolecular framework is formed by C–H ··O and C–H ··N hydrogen bonds (Table 2).

3. 2 IR analysis of complex 1

IR spectrum of **1** shows a broad absorption band at 3462 cm^{-1}, corresponding to the H ··O stretching of crystal water molecules in the complex. Asymmetric and symmetric COO^- stretching modes of the lattice 4-nph^{2-} anion were evidenced by very strong, slightly broadened bands at 1630 and 1342 cm^{-1}[9], which is consistent with the results of X-ray analysis.

3. 3 Thermal stability and powder X-ray diffraction (PXRD)

To confirm the phase purity of complex **1**, powder X-ray diffraction (PXRD) patterns were recorded for **1**, and it was comparable to the corresponding simulated patterns calculated from the single-crystal diffraction data (Fig. 4), indicating a pure phase of bulky sample.

In order to better understand the thermal stability of complex **1**, its thermal decomposition behaviors were investigated at 50～800 ℃ under nitrogen atmosphere (Fig. 5). The TG curve of **1** indicates no obvious weight loss from 25 and 171 ℃. Then a weight loss of 1.79% is observed from 171 to 299 ℃ due to the removal of one crystal water molecule (calcd. 1.91%). The TG curve presents a platform and the framework starts to decompose at 304 ℃.

3. 4 Photoluminescent properties

Luminescence property is very important in photochemistry and photophysics[10, 11]. So, in this study the solid-state photoluminescence spectra of **1** (Fig. 6) and 4-H_2nph, bib ligands were investigated at room temperature. When excited by 355 nm, **1** gives wide green emission with the maximum peak at 531 nm plus shoulder peak at 452 nm. We then investigated the emission spectrum of 4-H_2nph and bib ligands, and the results indicated that they do not emit any luminescence in the range of 400～800 nm. The significant fluorescence emission of **1** here could be tentatively assigned to the ligand-to-metal charge transfer (LMCT)[12]. For its strong fluorescent intensity, **1** appears to be a good candidate for novel hybrid inorganic-organic photoactive materials.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–O(3)	1.946(5)	Zn(1)–O(8)	1.942(5)	Zn(1)–N(3)	2.021(6)
Zn(1)–N(5)	2.009(6)	Zn(2)–O(2)	1.972(5)	Zn(2)–O(11A)	1.981(5)

Zn(2)–N(2)	1.987(6)	Zn(2)–N(9)	2.015(6)		
Angle	(°)	Angle	(°)	Angle	(°)
O(8)–Zn(1)–O(3)	126.4(2)	O(3)–Zn(1)–N(3)	107.3(3)	O(11A)–Zn(2)–N(7)	106.5(2)
O(8)–Zn(1)–N(5)	109.8(2)	N(5)–Zn(1)–N(3)	114.5(3)	O(2)–Zn(2)–N(9)	95.7(2)
O(3)–Zn(1)–N(5)	101.2(2)	O(2)–Zn(2)–O(11A)	103.4(2)	O(11A)–Zn(2)–N(9)	117.5(2)
O(8)–Zn(1)–N(3)	98.2(3)	O(2)–Zn(2)–N(7)	124.6(3)	N(5)–Zn(1)–N(9)	109.6(3)

Symmetry code: A: *x*+1, *y*, *z*

Table 2. Hydrogen Bonds for Complex 1

D–H ··A	d(D–H)	d(H ··A)	d(D ··A)	∠(DHA)	Symmetry codes
C(3)–H(3) ··O(5)	0.93	2.58	3.412(13)	148	*x*, 1+*y*, *z*
C(17)–H(17) ··O(11)	0.93	2.24	3.1676(10)	172	1+*x*, *y*, *z*
C(19)–H(19) ··O(1)	0.93	2.38	3.181(11)	145	1–*x*, 1–*y*, –*z*
C(24)–H(24) ··O(4)	0.93	2.56	3.406(12)	151	–*x*, 1–*y*, 1–*z*
C(27)–H(27) ··O(7)	0.93	2.40	3.267(10)	155	1–*x*, 1–*y*, –*z*
C(27)–H(27) ··O(12)	0.93	2.46	3.100(10)	127	1–*x*, 1–*y*, –*z*
C(32)–H(32) ··O(4)	0.93	2.54	3.354(11)	147	1+*x*, *y*, *z*
C(32)–H(32) ··O(12)	0.93	2.42	2.998(9)	120	1+*x*, *y*, *z*
C(35)–H(35A) ··O(10)	0.97	2.53	3.499(13)	176	–*x*, 1– *y*, 1–*z*
C(35)–H(35A) ··N(1)	0.97	2.62	3.534(13)	1563	–*x*, 1–*y*, 1–*z*
C(36)–H(36B) ··O(1W)	0.97	2.50	3.45(2)	167	1–*x*, –*y*, 1–*z*

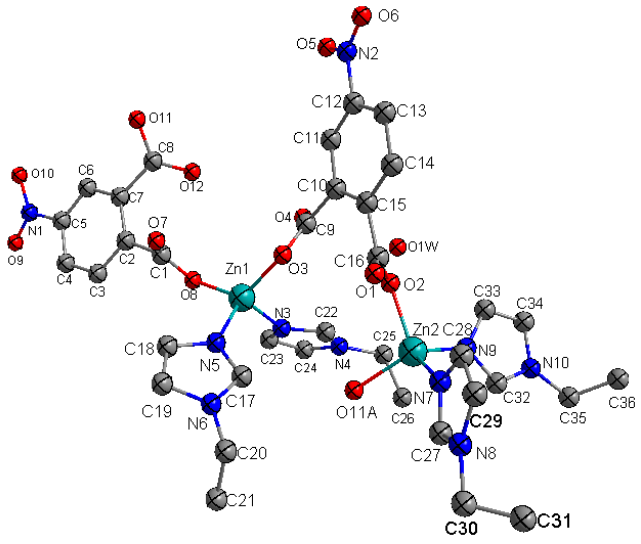

Fig. 1. View of the asymmetric unit of complex 1. All hydrogen atoms are omitted for clarity

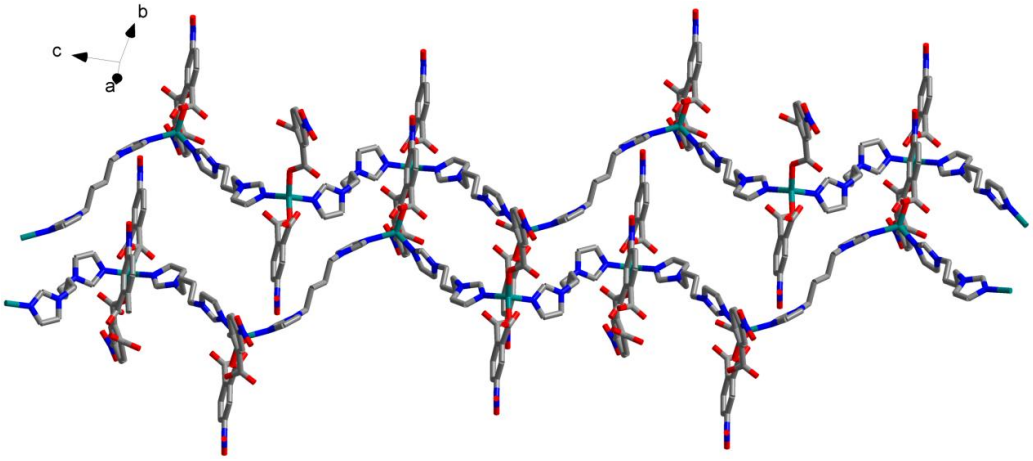

Fig. 2. View of the one-dimensional double chain of complex 1

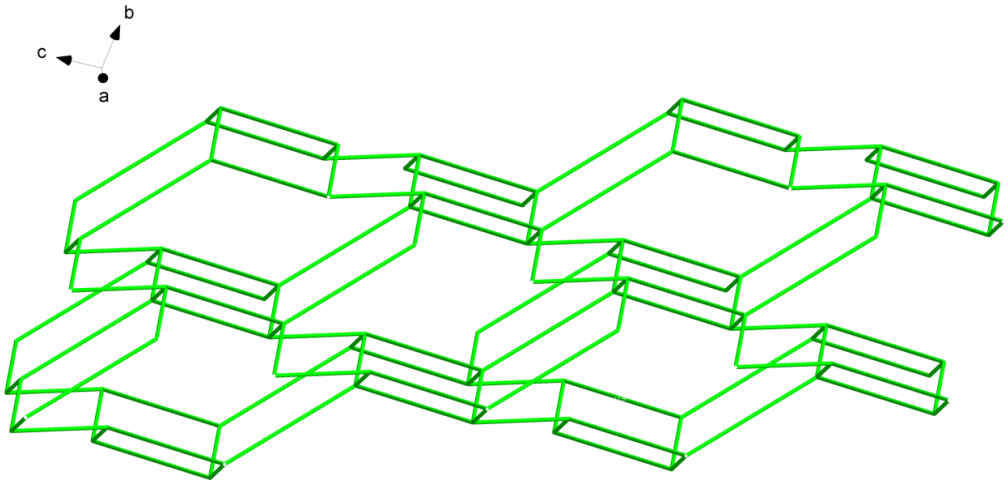

Fig. 3. Schematic view of the topology of complex 1

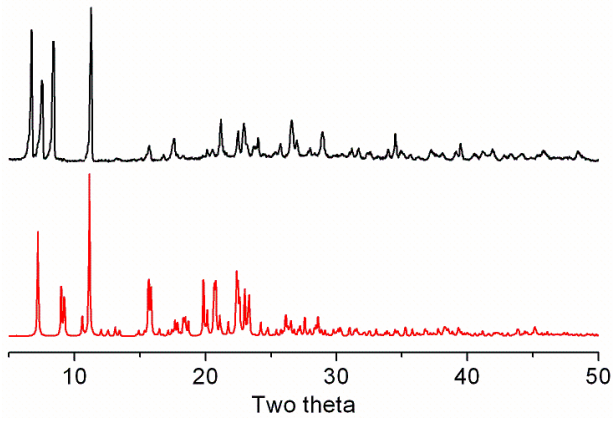

Fig. 4. PXRD analysis of the title complex: bottom-simulated, top-experimental

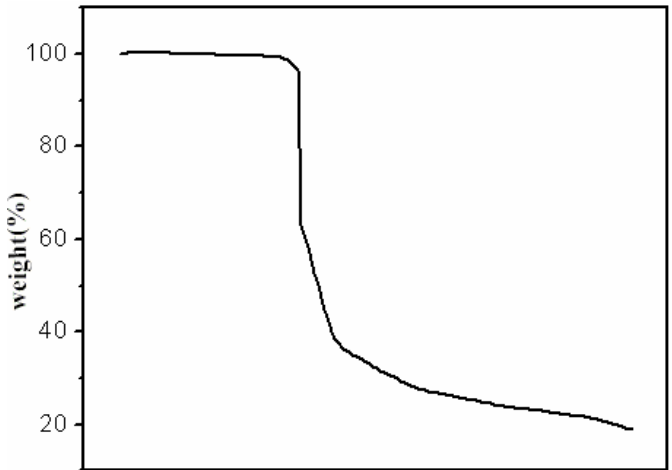

Fig. 5. TG curve of complex 1

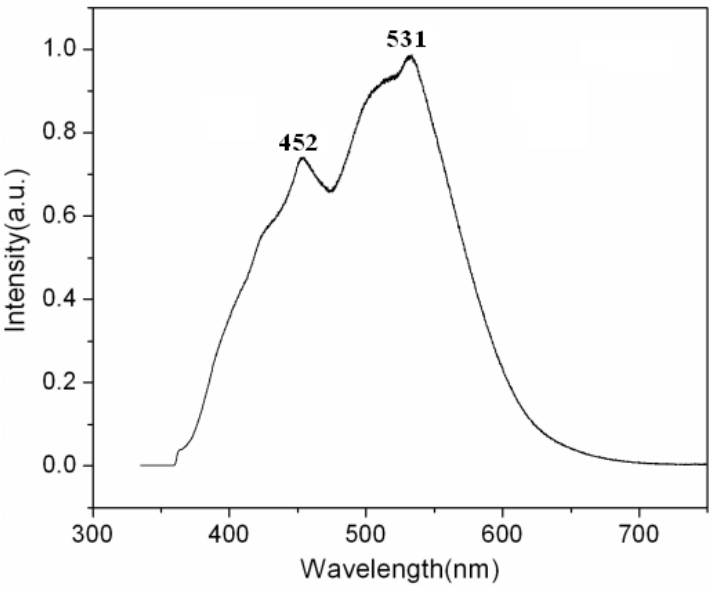

Fig. 6. Solid-state emission spectrum of 1 at room temperature

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A new complex $[Zn(4\text{-nph})(bib)]_{2n}\ nH_2O$ (**1**) has been obtained by the reaction of metal (Zn(II)), 1,4-bis(imidazol-1-yl)-butane (bib) with 4-nitrophthalic acid ($4\text{-}H_2nph$), and its crystal structure was determined by single-crystal X-ray diffraction analysis. **1** shows a three-dimensional framework, and is assembled into a supramolecular structure through intermolecular hydrogen bonds. The thermal stability and luminescent properties of **1** were also investigated.